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# THE ANALYSIS OF EFFLUENTS AND ENVIRONMENTAL SAMPLES FROM URANIUM MILLS AND OF BIOLOGICAL SAMPLES FOR URANIUM, RADIUM, AND POLONIUM

Public Health Service, Salt Lake City, Utah

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By

David E. Rushing

SUPPLEMENTARY MATERIAL

For Distribution at the Symposium on Radiological Health and Safety in Nuclear Materials Mining and Milling in Vienna, Austria, August 26-30, 1963

U. S. Department of Health, Education, and Welfare
Public Health Service
Bureau of State Services
Division of Water Supply and Pollution Control
Colorado River Basin Water Quality Control Project Laboratory
Salt Lake City, Utah

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# DETERMINATION OF URANIUM
## A Fluorimetric Method

by
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## PRELIMINARY PREPARATION OF SAMPLES

In order to obtain the maximum fluorescence from a sample containing uranium, it is necessary that the uranium exist in the hexavalent condition in the final melt. While the fusion process will oxidize the uranium, it is best that reducing substances, such as carbon, be oxidized before the fusion step is undertaken. That is, the solution of uranium should contain only inorganic substances or only organic substances which can be ignited easily in the fusion dish prior to the addition of the flux.

Dry ashing of biological samples in platinum is preferable to wet-ashing methods, but the latter find some applications. Dry ashing should be done at not over 500° C. In the case of urine, the aliquot (about 1 ml.) can be ashed in the fusion dish because separations are not normally required.

Some materials, such as ores and bone, should be put into solution in order to obtain a representative aliquot. Other samples, such as blood, will require removal of interferences (iron, in the case of blood). For removal of interferences, see (1, 2).

After evaporation, preliminary to fusion, the sample aliquot should not contain significant amounts of quenching metals. The aliquot should not contain more than a trace of nitrate, bisulphate, sulfuric acid, perchloric acid, perchlorates, nor any other substance which will attack platinum. With uranium-rich samples such as ores, uranium standard

solutions, and some mill process solutions, the use of nitric acid is quite permissible because the residue from a reasonable aliquot will be essentially weightless.

Because of the simplicity of the direct fluorimetric method, it is often applied to samples without separations and the recovery is checked by spiking. If quenching is significant, then separations are carried out.

## REMOVAL OF IRON (3)

1. Obtain the inorganic sample or ash in solution in 25 ml. 1:9 HCl. Transfer to a separatory funnel. Add 6 drops of 6% cupferron (in water). Add 10 ml. chloroform and shake 1 minute. Discard $CHCl_3$ layer.
2. Repeat the addition of cupferron, $CHCl_3$, and the extraction until the iron cupferrate no longer forms (judged by color of precipitates and extracts).
3. Finally extract several times with $CHCl_3$ to remove excess cupferron.
4. Draw aqueous layer into 50-ml. volumetric flask and dilute to mark. Mix.
5. Take suitable aliquot into fusion dish. Evaporate and ignite (gently) to oxidize any residual organic material. Proceed with fusion with flux.

## DETERMINATION OF URANIUM (2)

1. Obtain sample in an essentially inorganic solution in dilute HCl (in special cases, $HNO_3$ may be preferable).
2. Transfer a suitable aliquot to the platinum dish used for fusion. Evaporate to dryness. (Ignite, gently if organic material is present.)
3. Add 1.00 gram of flux. (Prepare by fusing and mixing, while molten,

45.5 g. $Na_2CO_3$, 45.5 g. $K_2CO_3$, and 9 g. NaF. Cool, grind to pass 10 mesh, and bottle.)

4. Hold the dish high over a Meker burner and gradually lower it until the flux melts. Keep the flux just molten. Do not heat any hotter than necessary and keep dish in oxidizing portion of the flame. Swirl flux in dish for 30 seconds, then place on a level triangle over a Bunsen burner which has been previously adjusted to just keep the flux molten. Allow sample to stay molten for an additional 90 seconds. Remove flame and allow 30 seconds for solidification. Cool on a porcelain plate for 60 seconds; transfer to a desiccator. After 30 minutes read the fluorescence of melt in a transmission-type fluorimeter.
5. From a calibration curve, determine the amount of uranium in the melt and calculate the uranium content of the sample after deducting the blank. (Uranyl nitrate in 1:99 nitric acid provides a suitable uranium standard when evaporated and fused like samples.)
6. If sample is to be spiked, the spiked sample may be carried through the entire procedure or it may be spiked after step 5 as described here. Reserve the melt on a clean numbered support (watch glass) in a desiccator. Rinse the platinum fusion dish and add the spike. (The spike should be large enough to give an accurate reading but, obviously, the sum of the spike and uranium in the sample must not exceed the range of the fluorimeter.) Evaporate to dryness, add the original reserved melt, re-fuse and read again as in step 4.

7. Calculate percentage recovery by use of the formula:

$$\% \text{ Recovery} = \frac{\text{Obs. U in Spiked Samp. - Obs. U in Unspiked Samp.}}{\text{U in Spike}} \times 100$$

If the % recovery is low (say, < 85%), separations should be considered.

## RECOVERY

Recovery data for urine are shown in Table I.

TABLE I

Recovery of Uranium from Dry-Ashed Urine
(1-ml. Sample)

| Number of Analyses | Micrograms Uranium per Liter of Urine | | | |
|---|---|---|---|---|
| | Added | Recovered | Average Deviation | Max. Deviation |
| 14 | 1 | 0.964 | 0.15 | 0.43 |
| 13 | 10 | 9.57 | 0.38 | 1.3 |
| 8 | 50 | 47.7 | 0.7 | 2.1 |
| 6 | 100 | 99.2 | 2.6 | 5.5 |

## SPECIAL EQUIPMENT AND REAGENTS

### Fluorimeter

Usually custom-built but commercial instruments are available. Sensitivity is generally important. Exact method is, to some extent, dependent upon this basic instrument. There are two general types--"transmission" and "reflecting."

### Fusion Dishes

Usually platinum and designed especially for fluorimeter. These vary greatly in capacity.

Flux

Type is dependent, to some extent, upon the type of fluorimeter. Transmission fluorimeters require that melt be removable from dish in one piece. Uniformity with respect to uranium content is extremely important in obtaining reproducible blanks.

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(3) Author's adaptation.

# THE DETERMINATION OF RADIUM-226
## A Simplified Emanation Technique

by
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## INTRODUCTION

The emanation method for determining radium-226 (hereinafter referred to as radium) is based upon measuring the radon-222 produced by the radium within a definite time interval. It is characterized by certain advantages such as sensitivity, specificity, and wide applicability. On the other hand, it is not as well adapted to routine use as are methods based on alpha counting of radium-226 itself. For samples of complex composition and referee work, the method is unexcelled. The need for reliable methods has been pointed out in a companion paper (8).

In order to obtain good results, it is necessary only to collect quantitatively the radium with a carrier, dissolve the radium and carrier, allow the solution to age in a closed vessel, remove the radon from solution, and count the radon in a suitable counter. The purpose of this paper is to describe simplified techniques and apparatus suitable for accomplishing that end. The paper presents the problems from a chemist's point of view.

During the past decade, there were several developments which made the determination of radium by the emanation method much more practical for laboratories which did not possess highly specialized and expensive equipment. The developments were in three distinct areas - de-emanation techniques, radon counting chambers, and scintillation counters. Simplification and progress in these areas have made it possible

to determine radium accurately at almost any reasonable concentration in almost any type of sample.

In 1953, Shandley (9) used fritted glass bubblers with stopcocks on each end as the containing vessels for the growth of radon from radium solutions. These were de-emanated by passing counting gas through the cold solutions at a controlled rate. Efficiency of de-emanation was very high. In 1957, a more convenient modification of Shandley's bubbler and efficiency data which paralleled those obtained by him were reported (5).

Scintillation cells can be substituted for ionization or pulse counting chambers which are used in the classical emanation methods. Scintillation counting cells for radon have been described by Van Dilla and Taysum (10), Kusnetz (6), and Lucas (7). Lucas' cell has evolved from that of Van Dilla and Taysum and is probably the best for laboratory use. The writers have further modified Lucas'cell (Figure 1) but their main changes have been in simplification of techniques rather than in the finished cell. Lucas used helium as the filling gas; the writers get satisfactory results with aged compressed air.

Basically, an alpha scintillation counter is less complicated than a proportional counter, which in turn is much more simple than a radon pulse counter (1, 3, 9). The simplicity stems from the fact that little or no amplification is needed for the electrical pulse associated with an alpha scintillation. The design and performance of a scintillation counter usually are centered around the photomultiplier tube and high voltage supply. Two- and three-inch flat-faced tubes are satisfactory for two-inch scintillation cells. The photomultiplier tube should be

protected from heat to reduce noise; though noise effects do not seem to be serious in alpha counting with the Lucas-type cell. The high voltage supply must be stable while furnishing the current required by the potential divider which supplies the required potentials to the dynodes of the photomultiplier tube.

## EQUIPMENT

### Scintillation Cells

Scintillation cells were prepared, with some modifications, according to Lucas. The cell is shown in Figure 1. The microstopcocks used by Lucas tend to leak; larger stopcocks are recommended. Also the inlet tubes protrude into the cells to avoid disturbance of the phosphor when air is admitted.

Sizing of the phosphor was carried out as described by Lucas. It was found to be simpler to apply the phosphor from a thick slurry rather than by spraying. A few drops of polystyrene dope per hundred ml. of solvent helped to prevent loosening of the phosphor; too much binder probably adversely affects the slope of the plateau. The thick slurry was added to the weighed Kovar® shell, which had its small end stoppered, and the shell was rotated as the slurry was poured out slowly. Rotation was continued until the solvent evaporated. After drying at room temperature the cell was reweighed and, if necessary, retreated until the even coating weighed 2.5 ± 0.2 grams.

Next, the cell was tapped rather sharply to dislodge any phosphor which might drop off after the cell was assembled. The stopcock was then inserted and cemented in. After the resin set, the coated windows were

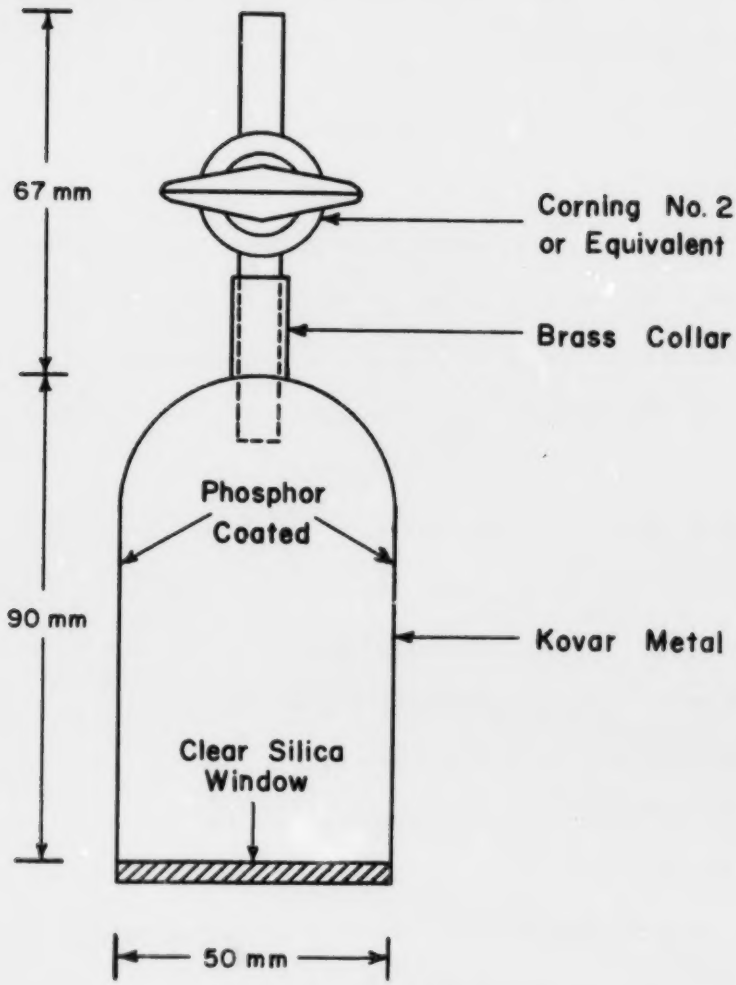


Figure 1. Scintillation Cell

cemented on. After the windows were firmly set, a coating of silver paint was applied between the lateral edge of the window and the Kovar® body to make an electrical connection.

Silica windows can be coated rather simply by heating them to red heat in an electric furnace, allowing them to cool to about 500° C., and churning in stannic chloride vapor in a tall beaker. The process does not take much time (one or two passes) and must be watched closely to avoid deposition of too thick a coating.

Cells prepared in the above manner give 290 - 338 counts per hour per micromicrocurie of radon plus decay products. The variation probably is caused mostly by nonuniformities in window coatings. Backgrounds on cells filled with aged compressed air varied from 6 to 15 counts per hour. The volume of a cell is about 140 ml.

The precision of the radon determination in the cells is illustrated by the data shown in Table I. Some of the results represent repeated deemanations of the same bubbler, while others represent replicate samples. In some cases the measurements were made at the same time or over a period of a few days. In other cases several weeks elapsed between measurements. The writers' experience indicates that an accuracy of about ±2% is attainable when statistical counting errors are reduced to insignificance.

The performance of the cells with low levels of radon can be judged by the data given in Table II. These data were collected in connection with breath radon work and represent radon which was adsorbed on charcoal and then desorbed into the scintillation cell. Thus the data include some extraneous errors (about -1.5%) which would not appear in a radium determination.

TABLE I

Results of Replicate Analyses and De-emanations of Samples

| Sample Type | µµg. Radium Found[a] | σ's (µµg. Radium) |
|---|---|---|
| | Replicate Analyses | |
| Silicate 1 | 13.9 , 14.1 , 14.0 | 0.3 , 0.2 , 0.2 |
| Silicate 2 | 16.7 , 16.8 | 0.2 , 0.2 |
| Silicate 3 | 24.1 , 25.0 | 0.5 , 0.4 |
| Silicate 4 | 50.9 , 50.8 | 0.8 , 0.6 |
| Silicate 5 | 73 , 76 | 0.8 , 1.1 |
| Uranium mill effluent 1 | 1.67, 1.64 | 0.05 , 0.04 |
| Corn, frozen | 0.03, 0.05 | 0.003, 0.01 |
| Potatoes, dried | 0.47, 0.47 | 0.01 , 0.01 |
| Potatoes, dried, spiked | 5.05, 5.38 | 0.03 , 0.03 |
| Beans, dried | 1.10, 1.21 | 0.01 , 0.01 |
| Beans, dried, spiked | 5.90, 6.08 | 0.04 , 0.04 |
| Bone, meal | 4.21, 4.25 | 0.03 , 0.03 |
| Bone, hog | 1.34, 1.68, 1.64[b] | 0.04 , 0.04, 0.03 |
| Bone, hog, spiked | 1015, 1028, 1002[b] | 6 , 3 , 4 |
| | Replicate De-emanations | |
| Standard radium solution 1 | 141.6 , 141.3 , 141.4 | 0.4 , 0.4 , 0.3 |
| Standard radium solution 2 | 14.4 , 14.6 | 0.1 , 0.2 |

TABLE I (Continued)

| Sample Type | µµg. Radium Found[a] | σ's (µµg. Radium) |
|---|---|---|
| | Replicate De-emanations | |
| Silicate 3 | 24.5 , 25.6 | 0.4 , 0.5 |
| Silicate 5 | 74 , 72 | 1 , 1 |
| Silicate 6 | 0.47, 0.47 | 0.01 , 0.01 |
| Silicate 7 | 7.7 , 7.9 | 0.3 , 0.1 |
| Silicate 8 | 8.9 , 8.5 | 0.2 , 0.1 |
| Silicate 9 | 11.50, 11.51 | 0.08 , 0.08 |
| Uranium mill effluent 2 | 0.93, 1.07 | 0.04 , 0.02 |
| Uranium mill effluent 3 | 2.60, 2.66, 2.79, 3.16 | 0.09 , 0.08, 0.12, 0.08 |
| Uranium mill effluent 4 | 3.28, 3.40, 3.48, 3.45 | 0.13 , 0.08, 0.09, 0.07 |
| Uranium mill effluent 5 | 5.78, 5.97[c] | 0.18 , 0.07 |
| Uranium mill effluent 6 | 5.93, 5.87, 6.08[c] | 0.20 , 0.07, 0.07 |
| Uranium mill effluent 7 | 8.6 , 8.8 , 8.9[c] | 0.2 , 0.1 , 0.1 |
| Uranium mill effluent 8 | 10.1 , 10.1[c] | 0.4 , 0.1 |
| Alfalfa, green | 102 , 107 | 1 , 1 |
| Apples, fresh | 0.21, 0.20 | 0.01 , 0.01 |
| Potatoes, dried, spiked | 5.00, 5.10 | 0.03 , 0.03 |

a The purpose of table is to show comparative values; to simplify table, units are not given. In some cases the figures represent radium in bubbler; in others the figures represent radium in a certain sized sample. In either case, the σ's reflect statistical counting errors; σ's are based on counting statistics only.

b Replicate samples treated by quite different chemical methods. These methods all showed 98-100% recovery of radium. The unspiked sample was to be used later with large spike so not much attention was paid to mixing. Values probably reflect heterogeneity of bone itself.

c The ages of solutions at counting and counting times were varied widely to accentuate any effects from radon-219 or radon-220. These particular samples contained thorium-227 and radium-223 in unfavorable ratios and were of the type which causes so much difficulty and uncertainty in direct radium-226 methods.

TABLE II

Determination of Low Levels of Radon (after Adsorption on and Desorption from Activated Charcoal)

| μμc. Radon | | Error,[b] |
|---|---|---|
| Taken | Found ± σ[a] | % |
| 0.049 | 0.047 ± 0.008 | - 4.1 |
| 0.053 | 0.054 ± 0.010 | + 1.9 |
| 0.147 | 0.134 ± 0.010 | - 8.8 |
| 0.148 | 0.136 ± 0.011 | - 8.1 |
| 0.153 | 0.129 ± 0.016 | -16 |
| 0.594 | 0.583 ± 0.015 | - 1.9 |
| 0.712 | 0.684 ± 0.015 | - 3.9 |
| 1.23 | 1.22 ± 0.018 | - 0.8 |
| 1.28 | 1.23 ± 0.019 | - 3.9 |
| 3.30 | 3.33 ± 0.055 | + 0.9 |
| 3.87 | 3.87 ± 0.033 | 0.0 |
| 4.95 | 4.83 ± 0.031 | - 2.4 |
| 4.96 | 4.81 ± 0.031 | - 3.0 |

a σ is based on counting statistics only.

b Includes an error of approximately -1.5% due to factors which are unrelated to the radon determination itself.

Radon Bubblers

The design of bubblers previously reported by the senior author has been modified further to be compatible with special chemical methods and the scintillation cell counting method for radon (5). See Figure 2. While many factors theoretically would affect the rate of removal of radon from a bubbler, the more important ones are: the volume of the bubbler; the relative volumes of the air space and the liquid; the nature, volume, rate of flow, and constancy of flow of the de-emanating gas; and the porosity, size, and uniformity of the fritted glass disc. Some of the factors are interrelated. No detailed study was made of the individual factors but the characteristics of the fritted glass disc are extremely important.

Table III indicates the efficiency of de-emanation of a bubbler which was selected at random. From the data, it would appear that a bubbler four times as large might be de-emanated with 99.8% efficiency. However, individual variations within a group of bubblers might cause decreased efficiency. The writers feel that a scale-up factor of two would be safe with the same volume of de-emanating gas.

When bubblers are used with 100 mg. $Ba^{++}$ and with samples which do not vary in radium content by a factor of more than 10 to 20, no cleaning other than a thorough distilled water rinse is required. Sulfuric-chromic acid should not be used for cleaning. Hot alkaline ethylenediaminetetraacetic acid solution was found to be satisfactory for general cleaning; a 10-minute treatment with hot 5% alcoholic KOH will remove the silicone grease from the stopcocks and the cement from

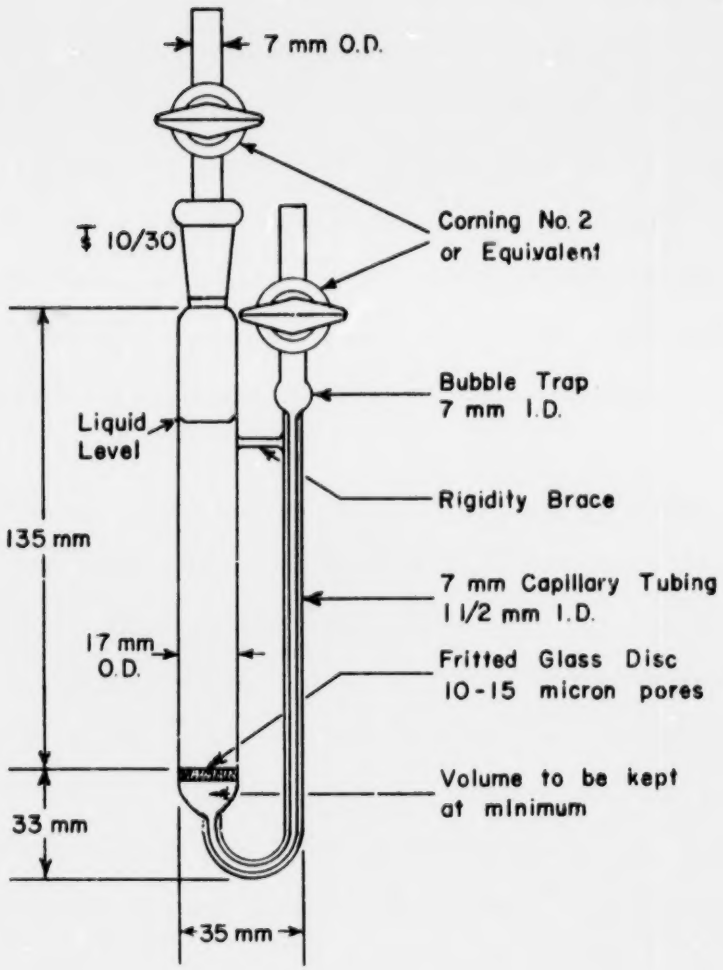


Figure 2. Radon Bubbler

TABLE III

Efficiency of De-emanation of a 27-ml. Radon Bubbler

| Fraction | Elapsed Time from Beginning of De-emanation, Minutes | | Volume of Air Passed, ml.[a] | Average Flowrate in ml. per min.[a] | µµc. Ra Found | Growth of Rn Since Previous Fraction, µµc. | µµc. Rn Found, Corrected | % of Total Rn Found |
|---|---|---|---|---|---|---|---|---|
| | Start | Finish | | | | | | |
| First | 0.00 | 6.12 | 36.1 | 5.9 | 3,993 | -- | 3,993 | 99.80 |
| Second | 7.25 | 11.83 | 34.9 | 7.6 | 8.5 | 2.9 | 5.6 | 0.14 |
| Third | 12.42 | 18.05 | 34.4 | 6.1 | 4.8 | 3.1 | 1.7 | 0.04 |
| Fourth | 18.35 | 23.12 | 34.6 | 7.3 | 3.3 | 2.6 | 0.7 | 0.02 |
| Totals | | | 140.0 | | | | 4,001.0 | 100.00 |

a Pressures in second, third, and fourth receivers were adjusted to predetermined values before use in order to simulate a de-emanation into a single receiving vessel.

the ₹ joint. The bubbler used to obtain the data in Table III was decontaminated with hot alkaline ethylenediaminetetraacetic acid and the radium remaining was not detectable.

Counter Adjustment and Performance

The experience and data presented in this paper were obtained with two types of custom-made counters. Both used grounded cathode circuits for the photomultiplier tubes and the output pulse was fed into a cathode-follower impedance changer which was housed with the PM tube. The first type of counter consisted of a high voltage supply, a Berkeley Model 2105 scaler, and the PM tube (RCA 6655A (2")) housing; these were in three separate housings. The second type of counter was contained in one cabinet; it used a Dekatron scaling system and a DuMont No. 6363 (3") PM tube.

Some arbitrariness is involved in determining the operating conditions of the entire system. The writers were interested in low-level activity and adjusted the counters to give a low cell background and at the same time to give reasonable counting efficiency. Pulse energy discrimination can be achieved by several adjustments: (a) the voltage applied to the PM tube, (b) the input sensitivity of the scaler, and (c) the gain of the preamplifier, if such adjustment is possible. The instruments used did not have the third adjustment.

The cell calibration value, electrical background, cell background, and plateau slope are functions of two (or three) adjustments. Fortunately, they are not all the same function; thus it is possible to reduce the electrical and cell backgrounds without drastically reducing the cell calibration figure. Plateau slopes of from 0.2 to 2.0% per hundred volts

have been obtained with individual instruments. To obtain the lowest possible backgrounds, it is necessary to count at the lowest practical voltage. An electrical background of two counts per hour is satisfactory and attainable. Electrical background is especially likely to arise in the PM tube, the preamplifier, and the high voltage supply.

## OPERATIONAL TECHNIQUES

### Preparation of Solution for Bubblers

A detailed procedure for obtaining the radium from a sample in solution will not be given, since such details are beyond the scope of this discussion and are given elsewhere (10). It is best to use a carrier; about 100 mg. barium is the carrier used by the writers. Radium is collected in a barium-radium sulfate precipitate by suitable chemical operations. The precipitate is fumed in platinum with phosphoric acid and heated just below red heat to drive off $SO_3$. The resulting glassy melt is dissolved by evaporating it with a crucibleful of 1:3 HCl on the steam bath. The residue is dissolved in about 6 ml. 1:5 HCl and transferred to the bubbler. The bubbler joints are rinsed, dried, coated with low-temperature cement, and sealed. If the radon is to accumulate for a short time, the bubbler should be de-emanated to establish the zero time precisely. The stopcocks are closed and the bubbler is set aside until the final de-emanation is to be done.

To prepare a standard bubbler proceed as follows: Close the inlet stopcock and add 1 ml. 10% (weight) barium chloride. Add about 5 ml. sulfate-free distilled water plus 0.5 ml. HCl and mix. Pipette the required amount of standard radium solution into the bubbler, add more

water, seal the bubbler, and mix by aeration. The amount of radium and the number of standard bubblers used depend upon the range of radium contents expected in samples and the number of cells to be calibrated at one time. For low-level work, 30 to 50 μμg. radium is a convenient amount for a standard. From such a standard, one can obtain about 5 μμc. radon by allowing growth for 16 to 24 hours.

De-emanation and Radon Determination

When the radon in the bubbler reaches the desired fraction of equilibrium it can be removed as follows:

Evacuate the scintillation cell and connect it to the bubbler and manometer as indicated in the diagram (Figure 3). With the needle valve open, adjust the valve pressure so that the air flows at a very low rate. Close the needle valve. Attach the bubbler outlet to the assembly and the inlet to the valve of an aged compressed air cylinder. Open the scintillation cell stopcock and observe on the manometer whether or not a leak is indicated. If there is no significant leakage, open the regulator needle valve and the inlet stopcock of the bubbler completely. Now carefully slightly open the outlet stopcock on the bubbler (using at first the displacement of droplets in the capillary inlet tube as a guide--not the bubbles through the frit) until the bubbling rate is satisfactory as judged from experience. When bubbling subsides, carefully open the outlet stopcock all the way and gradually raise the inlet pressure until suitable bubbling is maintained and until atmospheric pressure is eventually reached. A very slight vacuum is preferable to a slight pressure; with care, the pressure need not be further than 1 mm. Hg

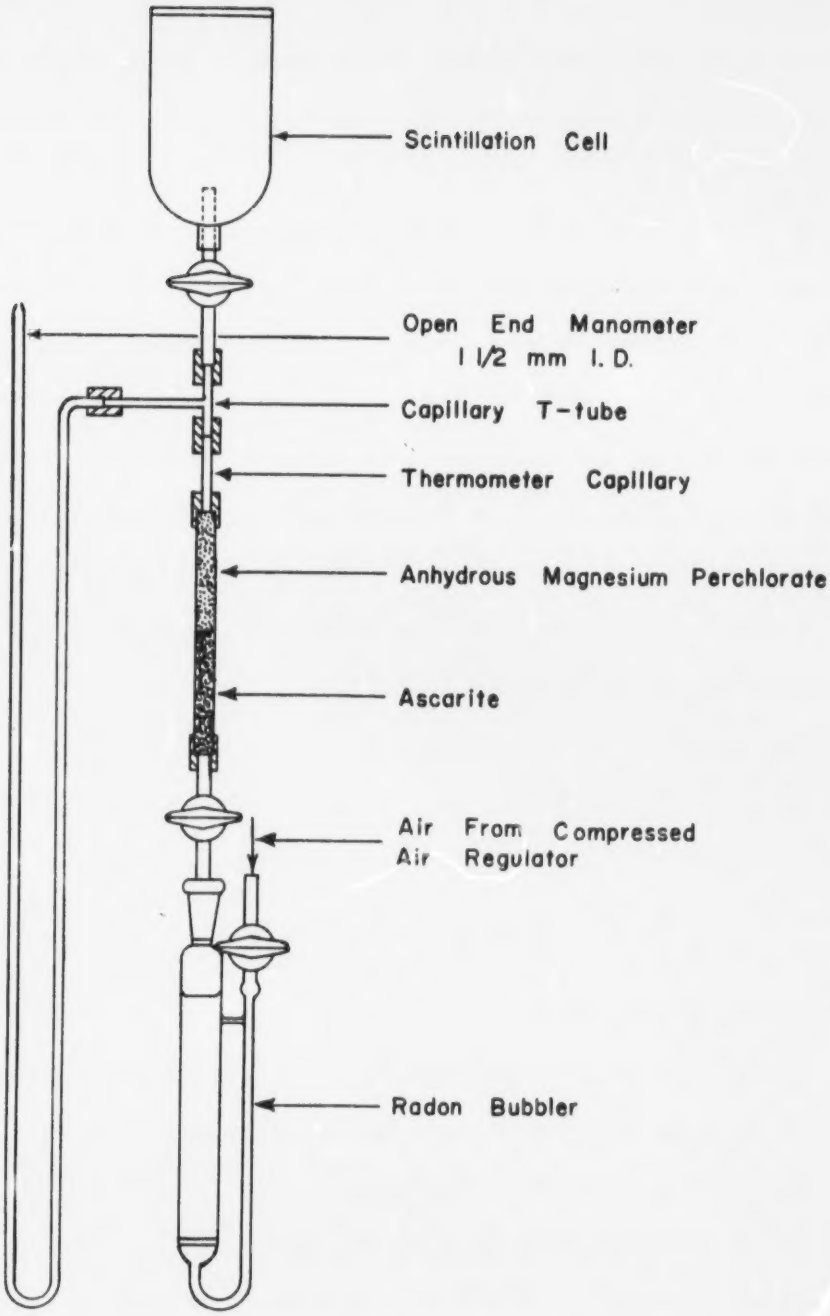


Figure 3. De-emanation Assembly

from atmospheric pressure. Close the stopcock on the cell, close the inlet bubbler stopcock, remove bubbler from assembly, apply slight suction to outlet of bubbler, and close outlet stopcock. Note time at which cell was closed and record.

Allow cell to stand 3 or 4 hours, depending upon accuracy desired, so that the enclosed radon and the newly formed decay products will come to transient equilibrium. Center the cell on the photomultiplier tube, attach ground wire, cover with the light-tight cover, allow five minutes for the light-activated phosphorescence to die out, and count. No oil is used for optical coupling of the PM tube and scintillation cell. Counting time depends upon the amount of radon and the statistical accuracy desired. The background of the cell and the reagent blank also affect the accuracy of the determination.

Calculation of Amount of Radium in Bubbler

For all practical purposes, one gram of radium equals one curie. The radium in the bubbler can be calculated from the formula

$$\mu\mu c.\ Ra = \frac{(R_s - R_b)}{R_c} \times \frac{1}{1-e^{-\lambda t_1}} \times \frac{1}{e^{-\lambda t_2}} \times \frac{\lambda t_3}{1-e^{-\lambda t_3}}$$

where $\lambda$ is the decay constant for radon,

$t_1$ is the time interval allowed for growth of radon from radium,

$t_2$ is the time interval between de-emanation and counting,

$t_3$ is the time interval of counting,

$R_s$ is the observed count rate of the sample,

$R_b$ is the (previously)observed background count rate of the scintillation cell,

and $R_c$ is the calibration constant of the scintillation cell in counts per unit time per μμc. of radon plus decay products.

All of the corrections can be obtained directly or indirectly from Table IV. The third correction factor is exceedingly close to $\frac{1}{e^{\frac{-\lambda t_3}{2}}}$; it can be combined with the second correction factor into a single factor to give $\frac{1}{e^{-\lambda(t_2 + \frac{t_3}{2})}}$ which will give a very close approximation to the result obtained by using the two separate exact factors.

A sample calculation may be helpful. Suppose the following data were collected:

$t_1$ = 13 d. 14 h. 6 m. $R_s$ = 199.2 ($\sigma_s$ = 3.5) c.p.h.

$t_2$ = 4 h. 15 m. $R_b$ = 9.3 ($\sigma_b$ = 0.8) c.p.h.

$t_3$ = 16 h. 30 m. $R_c$ = 335.4 ($\sigma_c$ = 2.3) c.p.h.

From Table IV

$1 - e^{-\lambda t_1} = 1 - 0.094,84 \times 0.899,69 \times 0.999,25 = 0.914,74$

$e^{-\lambda t_2} = 0.970,25 \times 0.998,11 = 0.968,42$

$\lambda t_3/(1-e^{-\lambda t_3}) = 1.063,58$ (by linear interpolation).

From these data,

$$\mu\mu c.\ Ra = \frac{(199.2 - 9.3)}{335.4} \times \frac{1}{0.914,74} \times \frac{1}{0.968,42} \times 1.06358 = 0.680.$$

Although its calculation is not given, $\sigma$ = 0.014 μμc. radium. See (4). The μμc. radium and $\sigma$ still need correction for the blank to give the correct figures for the sample.

TABLE IV

A. Decay of Radon (in Minutes, Hours, and Days)
B. Growth of Radon from Radium (in Days)
C. Multiplicative Factor for Correction of Radon Activity for Decay during Counting (in Hours)

(Based on 3.825 days as half-life of radon)

| Time | A. $e^{-\lambda t}$ | | | B. $1-e^{-\lambda t}$ | C. $\frac{\lambda t}{1-e^{-\lambda t}}$ |
|---|---|---|---|---|---|
| | Minutes | Hours | Days | Days | Hours |
| 0 | 1.000,00 | 1.000,00 | 1.000,00 | 0.000,00 | 1.000,00 |
| 1 | 0.999,87 | 0.992,48 | 0.834,27 | 0.165,73 | 1.003,72 |
| 2 | 0.999,75 | 0.985,01 | 0.696,00 | 0.304,00 | 1.007,54 |
| 3 | 0.999,62 | 0.977,60 | 0.580,65 | 0.419,35 | 1.011,39 |
| 4 | 0.999,50 | 0.970,25 | 0.484,42 | 0.515,58 | 1.015,16 |
| 5 | 0.999,37 | 0.962,95 | 0.404,14 | 0.595,86 | 1.018,98 |
| 6 | 0.999,25 | 0.955,71 | 0.337,16 | 0.662,84 | 1.022,83 |
| 7 | 0.999,12 | 0.948,52 | 0.281,28 | 0.718,72 | 1.026,65 |
| 8 | 0.998,99 | 0.941,39 | 0.234,66 | 0.765,34 | 1.030,51 |
| 9 | 0.998,87 | 0.934,31 | 0.195,77 | 0.804,23 | 1.034,36 |
| 10 | 0.998,74 | 0.927,28 | 0.163,33 | 0.836,67 | 1.038,23 |
| 11 | 0.998,62 | 0.920,31 | 0.136,26 | 0.863,74 | 1.042,10 |
| 12 | 0.998,49 | 0.913,38 | 0.113,68 | 0.886,32 | 1.045,97 |
| 13 | 0.998,37 | 0.906,51 | 0.094,84 | 0.905,16 | 1.049,88 |
| 14 | 0.998,24 | 0.899,69 | 0.079,12 | 0.920,88 | 1.053,79 |
| 15 | 0.998,11 | 0.892,93 | 0.066,01 | 0.933,99 | 1.057,69 |
| 16 | 0.997,99 | 0.886,21 | 0.055,07 | 0.944,93 | 1.061,61 |
| 17 | 0.997,86 | 0.879,55 | 0.045,94 | 0.954,06 | 1.065,54 |
| 18 | 0.997,74 | 0.872,93 | 0.038,33 | 0.961,67 | 1.069,49 |
| 19 | 0.997,61 | 0.866,36 | 0.031,98 | 0.968,02 | 1.073,44 |
| 20 | 0.997,49 | 0.859,85 | 0.026,68 | 0.973,32 | 1.077,40 |
| 21 | 0.997,36 | 0.853,38 | 0.022,25 | 0.977,75 | 1.081,37 |
| 22 | 0.997,24 | 0.846,96 | 0.018,57 | 0.981,43 | 1.085,35 |
| 23 | 0.997,11 | 0.840,59 | 0.015,49 | 0.984,51 | 1.089,34 |
| 24 | 0.996,99 | 0.834,27 | 0.012,92 | 0.987,08 | 1.093,33 |
| 25 | 0.996,86 | 0.827,99 | 0.010,78 | 0.989,22 | 1.097,34 |

TABLE IV (Continued)

| Time | A. $e^{-\lambda t}$ | | | B. $1-e^{-\lambda t}$ | C. $\frac{\lambda t}{1-e^{-\lambda t}}$ |
|---|---|---|---|---|---|
| | Minutes | Hours | Days | Days | Hours |
| 26 | 0.996,73 | 0.821,77 | 0.008,99 | 0.991,01 | 1.101,36 |
| 27 | 0.996,61 | 0.815,58 | 0.007,50 | 0.992,50 | 1.105,39 |
| 28 | 0.996,48 | 0.809,45 | 0.006,26 | 0.993,74 | 1.109,42 |
| 29 | 0.996,36 | 0.803,36 | 0.005,22 | 0.994,78 | 1.113,47 |
| 30 | 0.996,23 | 0.797,32 | 0.004,36 | 0.995,64 | 1.117,52 |
| 31 | 0.996,11 | 0.791,32 | 0.003,63 | 0.996,37 | 1.121,58 |
| 32 | 0.995,98 | 0.785,37 | 0.003,03 | 0.996,97 | 1.125,66 |
| 33 | 0.995,86 | 0.779,46 | 0.002,53 | 0.997,47 | 1.129,74 |
| 34 | 0.995,73 | 0.773,60 | 0.002,11 | 0.997,89 | 1.133,83 |
| 35 | 0.995,61 | 0.767,78 | 0.001,76 | 0.998,24 | 1.137,94 |
| 36 | 0.995,48 | 0.762,01 | 0.001,47 | 0.998,53 | 1.142,05 |
| 37 | 0.995,36 | 0.756,28 | 0.001,23 | 0.998,77 | 1.146,17 |
| 38 | 0.995,23 | 0.750,59 | 0.001,02 | 0.998,98 | 1.150,30 |
| 39 | 0.995,11 | 0.744,94 | 0.000,85 | 0.999,15 | 1.154,44 |
| 40 | 0.994,98 | 0.739,34 | 0.000,71 | 0.999,29 | 1.158,59 |
| 41 | 0.994,85 | 0.733,78 | 0.000,59 | 0.999,41 | 1.162,75 |
| 42 | 0.994,73 | 0.728,26 | 0.000,50 | 0.999,50 | 1.166,92 |
| 43 | 0.994,60 | 0.722,78 | 0.000,41 | 0.999,59 | 1.171,09 |
| 44 | 0.994,48 | 0.717,34 | 0.000,34 | 0.999,66 | 1.175,28 |
| 45 | 0.994,35 | 0.711,95 | 0.000,29 | 0.999,71 | 1.179,47 |
| 46 | 0.994,23 | 0.706,59 | 0.000,24 | 0.999,76 | 1.183,68 |
| 47 | 0.994,10 | 0.701,28 | 0.000,20 | 0.999,80 | 1.187,89 |
| 48 | 0.993,98 | 0.696,00 | 0.000,17 | 0.999,83 | 1.192,12 |
| 49 | 0.993,85 | 0.690,77 | 0.000,14 | 0.999,86 | 1.196,35 |
| 50 | 0.993,73 | 0.685,57 | 0.000,12 | 0.999,88 | 1.200,60 |
| 51 | 0.993,60 | 0.680,42 | 0.000,10 | 0.999,90 | 1.204,85 |
| 52 | 0.993,48 | 0.675,30 | 0.000,08 | 0.999,92 | 1.209,11 |
| 53 | 0.993,35 | 0.670,22 | 0.000,07 | 0.999,93 | 1.213,38 |
| 54 | 0.993,23 | 0.665,18 | 0.000,06 | 0.999,94 | 1.217,66 |
| 55 | 0.993,10 | 0.660,18 | 0.000,05 | 0.999,95 | 1.221,95 |
| 56 | 0.992,98 | 0.655,21 | 0.000,04 | 0.999,96 | 1.226,25 |
| 57 | 0.992,85 | 0.650,28 | 0.000,03 | 0.999,97 | 1.230,56 |
| 58 | 0.992,73 | 0.645,39 | 0.000,03 | 0.999,97 | 1.234,88 |
| 59 | 0.992,60 | 0.640,54 | 0.000,02 | 0.999,98 | 1.239,21 |
| 60 | 0.992,48 | 0.635,72 | 0.000,02 | 0.999,98 | 1.243,54 |

Isotopic Interferences

The senior author has observed what appeared to be radium-224 and radium-228 in uranium minerals. Difficulties experienced with uranium mill effluents have led to the use of an emanation method for radium-226. For the last nine years, such a method has been used by the writers on uranium mill effluents and other problem samples. For about five years, the method has been used exclusively for radium-226.

Under certain circumstances the ratios of radium-223 and of radium-224 to radium-226 may deviate from those found to occur naturally in uranium minerals and ores. Ebersole and others (2) have drawn attention to such deviations in the ratio of radium-223 to radium-226 existing in uranium mill effluents.

It is possible to calculate maximum effects which could be produced in an emanation method by the radon isotopes (actinon and thoron) formed from unit activities of radium-223 and radium-224. Radium-228 does not produce a radon isotope directly. Actually, it is the alpha emitters, formed by long-lived decay products of the radon isotopes, which cause the interference. Table V gives the calculated theoretical maximum effects of unit initial activities ($N_o\lambda_1$) of radium-223 and radium-224. Because of the short halflives of the actinon and thoron, their initial activities can be assumed to be unity also. The calculations also take into account all actinon and thoron produced during a 20-minute de-emanation period. Columns headed $\alpha_t/N_o\lambda_1$ show the total relative activity due to all the alpha emitters to the end of the particular series. The next column shows what this activity amounts to in terms of apparent radon-222. An example may be helpful. Suppose that the ratio of radium-223 to radium-226

TABLE V

Calculated Maximum Effects of Decay Products of Radium-223 and Radium-224 in Emanation Methods

| Time, Hours[a] | Radium-223 ($N_o\lambda_1$ = 1.000) | | Radium-224 ($N_o\lambda_1$ = 1.000) | |
|---|---|---|---|---|
| | $\frac{\alpha_t}{N_o\lambda_1}$[b] | Apparent Relative Rn-222 Activity | $\frac{\alpha_t}{N_o\lambda_1}$[b] | Apparent Relative Rn-222 Activity |
| 4 | 0.0038 | 0.0013 | 0.0178 | 0.0061 |
| 5 | 0.0012 | 0.0004 | 0.0167 | 0.0058 |
| 6 | 0.0004 | 0.0001 | 0.0156 | 0.0054 |
| 7 | 0.0001 | 0.0000 | 0.0146 | 0.0051 |
| 8 | 0.0000 | | 0.0137 | 0.0049 |
| 9 | | | 0.0128 | 0.0046 |
| 10 | | | 0.0120 | 0.0043 |
| 12 | | | 0.0105 | 0.0038 |
| 14 | | | 0.0092 | 0.0034 |
| 16 | | | 0.0081 | 0.0030 |
| 18 | | | 0.0071 | 0.0027 |
| 20 | | | 0.0062 | 0.0024 |

a Measured from time of de-emanation.

b Includes decay products from radon-219 or radon-220 at equilibrium with corresponding radium isotope plus those formed during the de-emanation which was assumed to last 20 minutes. Efficiency of transfer of radon isotope and its decay products was assumed to be 100%.

is 20:1 at the time of de-emanation and that the isotopic mixture of actinon and radon-222 is counted for two hours four hours after de-emanation. The apparent radon-222 would be less than 20 x 0.0004 + 1.00 = 1.008 as compared to the correct value 1.000. The interference from actinon can be reduced drastically by suitable scheduling of the de-emanation and counting. Effects from thoron are more serious. By taking advantage of the facts that both isotopes are short lived and that their decay products are solids, one may reduce their interference to insignificance by aging the radon isotopes in another vessel prior to transferring them to the counting container.

Blanks and Backgrounds

Reagent blanks plus contamination from the air can be expected to average around 0.05 μμg. radium with a range of 0.02 to 0.08 μμg. radium. With high activity samples some contamination of the blanks occurs and they may reach a level above 0.10 μμg. radium. If purification of the reagents is carried out, contamination from that source can be reduced to insignificance. Cell backgrounds are equivalent to from 0.02 to 0.05 μμc. radon and vary considerably among themselves. No practical way of reducing the cell background without major redesign is apparent to the writers.

## CONCLUSIONS

The apparatus, equipment, and technique described are suitable, convenient, and economical for the determination of radium at levels of about $5 \times 10^{-14}$ g. or more per sample. By suitable chemical manipulations,

the radium can be isolated from almost any type of sample with chemical yields of over 99.5%. The precision and accuracy are both limited by the radon determination. The latter is accurate to ±2% if enough counts are observed to render statistical variations insignificant; in routine determinations, the error may be somewhat greater.

Naturally occurring isotopes of radium, radium-223 and radium-224, interfere slightly because of the deposition of their alpha-emitting decay products within the scintillation cell. Calculated maximum interferences of the two isotopes are given. The interferences are much less than would be encountered from these isotopes in a proportional counter type of radium-226 determination. By using a somewhat more involved technique, one can reduce the isotopic interferences to insignificance, even though very high ratios of other radium isotopes to radium-226 exist.

Analyses of mill effluent samples which contained thorium-227 and radium-223 in unusually high ratios are shown in Table I. These analyses give experimental support to the conclusion that isotopic interferences are not serious.

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# THE DETERMINATION OF RADIUM-226 IN SILICATES
## A Rapid Isolation Method

by
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## INTRODUCTION

The Colorado River Basin Water Quality Control Project of the Division of Water Supply and Pollution Control, the Division of Radiological Health, and the Division of Occupational Health of the Public Health Service and many others are engaged in studies in which exposure to radium-226 (hereinafter referred to as radium) plays a major role. Many of the samples taken in these studies are siliceous in nature (e.g., sediments, uranium ores and tailings, and filter sands from water treatment plants) or, at least, contain silicates as a minor constituent (e.g., feces, foods, bone, and aquatic biota). Many accurate analyses of such samples are needed to evaluate pollutional problems and human radiation exposure. Such analyses are also of great interest to geologists and geochemists. Because of legal as well as research implications, methods must be highly specific and accurate at radium concentrations ranging from natural levels (ca. 0.1 to 1.5 μμg. Ra per g.) to several hundred or thousand micromicrograms of radium per gram of sample. A rapid and accurate radium analytical method has been developed for these types of samples and is presented here.

In the field of water pollution control, accurate data permit the calculation of radium balances for uranium mills (12). In the

Animas study, Tsivoglou et al. concluded that much of the dissolved radium in river water arises from spent ore solids discharged from mills, rather than from the dissolved radium discharged directly with the mill effluents (13, 14). Thus, a knowledge of the radium contents of sediments and other solids is of great importance in evaluating radium sources in water pollution work.

Acid-insoluble siliceous materials customarily are obtained in solution by (a) fusion with an alkaline flux such as sodium carbonate, (b) treatment with HF using $HClO_4$, $H_2SO_4$, $HNO_3$, HCl, or $H_3PO_4$ to displace any residual HF, and (c) a combination of these two methods (4). Method (a) has the advantage of usually accomplishing complete decomposition of the silicates, but the melt obtained is not completely soluble in acids because of the precipitation of silicic acid. Method (b) removes the silica (if the silicates are attacked by HF) but decomposition is usually not as complete as with method (a).

Analyses for radium are different from most other analyses in that a trace of an insoluble residue or precipitate may contain nearly all the radium, especially if that precipitate happens to act as a carrier for radium. Therefore, it is of the utmost importance that the precipitate or residue be dissolved in the initial decomposition or, at worst, be carried along so that it may be dissolved in a subsequent stage of the analysis. To attain this end, it is better to add a suitable amount of barium carrier near the beginning of the analysis and to recover this quantitatively as the sulfate. The barium sulfate will contain almost all of the radium. What constitutes a suitable

amount of barium will depend upon several factors: (a) the method of determination of the radium, (b) the amount of radium to be determined, and (c) the chemical techniques employed for the isolation of the barium-radium sulfate. If the radium is to be determined by the emanation method, a decigram or more of barium can be used. If the radium is present in such minute amounts that an aliquot cannot be taken and the radium is to be determined by alpha counting in a proportional counter, then the amount of barium must be kept at a minimum (a few milligrams) in order to avoid excessive losses of alpha counts due to self-absorption in the barium sulfate precipitate. A satisfactory emanation method requires that the radium be in solution and that no significant radium-bearing precipitate be present. In practice this latter statement is tantamount to requiring a nearly clear solution when large amounts of barium are present or a clear solution when little or no barium is present. In the latter case, the solution is more sensitive to the presence of sulfate. If the radium is to be determined in a proportional counter, a clear solution may be needed, but this will depend upon the proposed method of purification.

On ore residues Wamser et al. (15) have used a $H_3PO_4$ - HF decomposition which produces a clear solution. Their samples were high in radium so that no severe limitation was placed on the maximum amount of barium used. Their purification process requires a relatively large amount (10 mg.) of barium to render solubility losses negligible. Such a decomposition, assuming complete solution, should be suitable for

dissolving samples prior to determining radium by the emanation method. The decomposition method removes no radioactive substances, except radon and perhaps polonium.

Nicholson has reported the use of a sodium carbonate-borax flux in iron determinations which has the unusual advantage of preventing immediate precipitation of silicic acid even in strongly acid solutions (9). Such a solution may be boiled, filtered, and kept sometimes for several days without precipitation of silicic acid. By combining adaptations of Nicholson's fusion method with the phosphoric acid method of Wamser et al., the writers were able to combine the advantages of both methods into a rapid method for isolating radium from siliceous materials. It is expected that the resulting method will find applicability to a much wider variety of silicates than would the $H_3PO_4$ - HF method alone.

## EXPERIMENTAL AND RESULTS

### Preparation of Flux

The special flux is prepared as follows:

Weigh out 30 mg. barium sulfate, 65.8 g. potassium carbonate, 50.5 g. sodium carbonate, and 33.7 g. sodium tetraborate decahydrate and mix well in a large (500 ml.) platinum dish. Heat cautiously until the water is expelled; finally fuse the contents of the dish and mix thoroughly by swirling. Let the flux cool and grind it in a porcelain mortar to pass a 10-mesh screen or finer. It is advisable to keep an uncontaminated mortar and screen especially for this purpose.

Nicholson's original flux is sometimes desirable because of solubility or radioactivity considerations. It can be prepared by

fusing together sodium carbonate and sodium tetraborate in the ratio 3:1 (9). Barium sulfate is added, if the flux is to be used for radium analyses.

Working Procedure

The working procedure is as follows:

1. Weigh a one-gram sample of the siliceous substance in a platinum crucible or dish. Ignite overnight at 500° C. if judged necessary because of the presence of sulfides or organic matter. If more than traces of heavy metals are present, the preliminary ignition should be carried out in porcelain.
2. Mix sample with 8 grams flux. Fuse over a burner. Heat at a rate which will prevent spattering.
3. Cool crucible and place it in a covered 250-ml. beaker containing 120 ml. water, 20 ml. sulfuric acid, and 5 ml. 3% hydrogen peroxide. (The melt dissolves in a few minutes.) Note the intensity of the yellow color produced by titanium if it is present.
4. When melt is dissolved, rinse, remove, and reserve crucible (without cleaning). Precipitate barium sulfate slowly by adding from a burette 50 ml. barium chloride solution (2 mg. $Ba^{++}$ per ml.) while stirring vigorously.
5. Let stand at room temperature overnight. Add more peroxide, if needed. (Judge need by decreased intensity of yellow color.)
6. Filter through membrane filter and wash several times with 0.5% $H_2SO_4$.

7. Transfer the barium sulfate to the original platinum vessel with a fine stream of water (or carefully ignite the membrane filter in the vessel after moistening with a few drops of 10% ammonium sulfate to avoid conflagration). Add 0.5 ml. HF.
8. Evaporate to dryness and cautiously ignite over a burner.
9. Add 20 drops (1 ml.) $H_3PO_4$ and heat on hot plate at 200° C. and raise the temperature gradually to 300 - 400° C. Maintain this temperature for about 30 minutes.
10. Heat carefully over a small burner until copius fumes are no longer evolved. During this stage, swirl the crucible to cover all areas with the hot $H_3PO_4$. Finally, heat until the $H_3PO_4$ clears (just below redness). Be sure that all barium sulfate dissolves.
11. Cool the crucible. Fill it with 1:3 HCl and evaporate on the steam bath until the free acid is removed. Barium chloride will crystallize.
12. The residue of barium chloride and phosphoric acid is ready for processing in a way which is suited to the method selected for determining the radium. The radium isolation method is particularly compatible with the emanation method which is recommended. To prepare residue for the emanation method, add 6 ml. 1:5 HCl, warm, and transfer to a bubbler with suitable rinsing of crucible with water (about 11 ml.) (11).

If filter papers are to be used in Step 6, it is better to precipitate the barium sulfate from boiling solution in Step 4. Hot digestion for 60 to 90 minutes will be required to render the precipitate coarse

enough to be retained on paper. More hydrogen peroxide should be added just before filtration. Tests indicate that both hot and cold precipitation-digestion methods give satisfactory results.

The volume of HF used in Step 7 is normally enough, however more will be required if unusual amounts of silica are present.

Nitric acid can be used instead of hydrochloric acid in Steps 11 and 12 and is sometimes preferable. Because of the quite limited solubility of barium nitrate, the nitric acid concentration in Step 12 should be reduced to about 1:99.

Recoveries and Losses of Radium

While a vast amount of work has shown the coprecipitation of radium with barium sulfate in pure solutions to be very complete (1, 2, 3, 6, 10), the analytical method presented here was tested in order that unsuspected interferences could be ruled out. Two approaches were feasible in the present work: (a) to determine the radium which was not coprecipitated and (b) to determine the recovery of known amounts of radium added to analyzed samples. Approach (a) is preferred by the writers since it involves a direct measurement of the loss. With approach (b), all errors appear as lost (or gained) radium. Approach (b) proves nothing about the radium recovery from actual samples unless the recovery is poor. In this work, both techniques were used, but emphasis was on approach (a).

The filtrates at Step 6 from various types of samples were analyzed for radium (after adding the radium recovered from the original glassware) by coprecipitating with an additional 100 mg. $Ba^{++}$ and going through the

remainder of the procedure. The same crucibles (uncleaned) were used as had been used for the main barium-radium sulfate precipitates. Table I shows the results of the analyses of the first and second barium-radium sulfate precipitates. In the range covered, it is highly probable that a nearly constant percentage of the radium would be lost. The samples containing the larger amounts of radium should give the percentage loss more accurately than those containing less radium because of the improved accuracy in measuring the radium in the second precipitate. Thus, the true loss is probably in the range of 0.2 to 0.3%, but experimental errors in radon measurements make it appear to be as high as 2.8%.

Samples containing suspected problem elements and silicate samples were spiked with radium and analyzed by the method. The recoveries are shown in Table II. Some of the silicates contained slight (milligram) precipitates in varying amounts and the known zirconium sample contained a very large precipitate which was filtered off and analyzed separately. Comparisons of the various samples show that the recoveries are essentially the same for all spiked silicates and suspected interferences. Recoveries are quite satisfactory (99 ± 3%), but are not as good as the coprecipitation loss data indicate they should be (ca. 99.5%). The additional losses might be due to mechanical losses, to error in measurement of the radon, or to the radium's being in a non-emanating (i.e., insoluble) form. The writers do not believe the first and last reasons to be significant. The measurement of the radon appears to be the most likely source of significant error. From other work, the writers have found the error in radon measurements to be as much as ±2.5% exclusive of statistical counting errors.

TABLE I

Losses of Radium in Proposed Method
as Determined by Analysis of Filtrates

| Type of Sample | No. of Samples | Range of Radium Content, µµg./gram | Percentage of Radium Found in Second Precipitate | |
|---|---|---|---|---|
| | | | Range | Average |
| Filter | 2 | 0 to 3.3 | 0.00 to 1.2 | 0.60 |
| Sands | 5 | 4.1 to 29.0 | 0.18 to 0.74 | 0.42 |
| Top Soils | 5 | 0 to 4 | 0.00 to 0.86 | 0.17 |
| Muds | 2 | 0 to 3.9 | 2.0 to 2.8 | 2.4 |
| | 9 | 20 to 725 | 0.10 to 0.30 | 0.20 |

TABLE II

Analyses of Various Natural and Synthetic Samples;
Recovery of Added Radium (10-μμg. Level)

| Sample | μμg. Radium Added | μμg. Radium Present | μμg. Radium Found | σ as μμg. Radium | % Recovery of Total Radium |
|---|---|---|---|---|---|
| 5100 (Mud) | None[a] | -- | 2.44 | 0.02 | -- |
| | None[a] | -- | 2.54[d] | 0.02 | -- |
| | 10.17[a] | 12.66 | 12.40[d] | 0.10 | 97.9 |
| | 10.17[a] | 12.66 | 12.50[d] | 0.11 | 98.7 |
| 5197 (Top Soil) | None[b] | -- | 1.80 | 0.02 | -- |
| | None[b] | -- | 1.81[d] | 0.02 | -- |
| | 10.17[b] | 11.97 | 11.68[d] | 0.09 | 97.6 |
| | 10.17[b] | 11.97 | 11.60[d] | 0.08 | 96.9 |
| 5202 (Filter Sand) | None[c] | -- | 2.84 | 0.02 | -- |
| | None[c] | -- | 2.86[d] | 0.02 | -- |
| | 10.17[c] | 13.02 | 12.69[d] | 0.09 | 97.5 |
| | 10.17[c] | 13.02 | 12.61[d] | 0.09 | 96.9 |
| Radium thru | 10.17 | 10.18 | 9.93 | 0.09 | 97.5 |
| Entire Process | 10.17 | 10.18 | 10.18 | 0.09 | 100.0 |
| Blank | None | -- | 0.013 | 0.003 | -- |
| Calcium,[e] 200 mg. | 10.17 | 10.18 | 10.40 | 0.09 | 102.2 |
| Titanium,[e] 50 mg. | 10.17 | 10.18 | 10.40 | 0.09 | 102.2 |
| Zirconium,[e] 10 mg. | 10.17 | 10.18 | 10.04[f] | 0.06 | 98.6 |
| | | | 0.12[g] | 0.006 | 1.2 |
| Nobium,[e] 10 mg. | 10.17 | 10.18 | 10.30 | 0.08 | 101.2 |
| Tantalum,[e] 10 mg. | 10.17 | 10.18 | 10.11 | 0.10 | 99.3 |
| Tin,[e] 10 mg. | 10.17 | 10.18 | 10.23 | 0.08 | 100.5 |
| | | | | Average | 99.1 |

a Very slight turbidity in bubbler.
b Slight turbidity in bubbler. Estimated twice that in a.
c Some turbidity in bubbler. Estimated three times that in a.
d Filtered precipitates from the six spiked samples 5100, 5197, and 5202. Combined and analyzed for radium. The combined precipitate weighed 4.7 mg. and held only 0.05% of the total radium present.
e Contained 0.57 gram $KH_2PO_4$ also.
f Radium found in phosphoric acid solution after filtering off large zirconium phosphate precipitate.
g Zirconium phosphate precipitate processed and analyzed as separate sample.

All data given were obtained by emanation methods. Two methods were employed for determining radon. Scintillation counting was used for all samples which were suspected of containing small or moderate amounts of radium (i.e., 0 - 30 μμg. per g.). An ionization current method was employed for samples suspected of containing larger amounts of radium. For apparatus and methods, see Lucas (7), Holaday et al. (5), and Rushing et al. (11).

Nonradioactive Interferences

Any element which is coprecipitated with barium sulfate and forms an insoluble compound in dilute phosphoric acid is likely to cause trouble because of precipitation in the final solution (Step 12). Elements soluble in the final solution cause no difficulty even if coprecipitated by barium sulfate. The following elements in ten-milligram amounts are soluble in the final solution (phosphoric acid plus hydrochloric acid): lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, zinc, cadmium, mercury, iron, cobalt, nickel, copper, manganese, bismuth, lanthanum, yttrium, and elements 59-71 (except promethium). When the hydrochloric acid was replaced by nitric acid in the final solution, the following elements were soluble in ten-milligram quantities: lead, vanadium, arsenic, selenium, tellurium, silver, yttrium, and elements 59-71 (except promethium). Chemical considerations led to the use of nitric acid in the preparation of some of these test solutions; undoubtedly vanadium, arsenic, selenium, and tellurium would have been soluble had hydrochloric acid been used.

At the ten-milligram level, three elements caused difficulties which could be easily remedied as shown below:

Antimony dissolved in 17 ml. hot 1:16 hydrochloric acid (plus phosphoric acid) but 1:9 hydrochloric acid was required to keep it in solution when cooled.

Cerium(IV) precipitated on dilution to 17 ml. 1:16 nitric acid, but after conversion to the chloride and reduction with hydroxylamine hydrochloride, it remained in solution in 17 ml. 1:16 hydrochloric acid (plus phosphoric acid).

Thallium formed a gel on dilution to 17 ml. 1:16 hydrochloric acid or nitric acid; it remained in solution in 17 ml. 5:12 perchloric acid.

The following elements in ten-milligram amounts yielded large insoluble residues in the final solution (hydrochloric plus phosphoric acids): aluminum, gallium, titanium, zirconium, germanium, tin, chromium(III), and chromium(VI). Indium produced a residue of a few milligrams.

The previous preliminary tests indicated which elements were likely to cause difficulties when carried through the working procedure. Reasonable amounts of various elements were spiked with 0.57 grams potassium dihydrogen phosphate and carried through the entire procedure. (Phosphate is a common constituent of actual samples.) Ten-milligram quantities of tungsten, molybdenum, gallium, thorium, and germanium

caused no difficulties. Niobium, tantalum, and tin behaved anomalously. When spiked with radium in a separate test (hydrogen peroxide used), these three elements did not precipitate in the final solution; when done in an unspiked test (hydrogen peroxide omitted), they did precipitate. This lack of agreement is believed to be related to the nonreproducible behavior of phosphoric acid upon being dehydrated. The problem was not pursued further because of the rarity of the three elements involved. In the same tests zirconium and titanium precipitated in the final solution if hydrogen peroxide was omitted; only zirconium precipitated if hydrogen peroxide was used. The zirconium precipitate did not contain significant amounts of radium (see Table II).

To determine the effect of small (milligram) phosphatic precipitates in the final solution, precipitates from fourteen routine samples were combined and analyzed for radium. The combined precipitates contained 0.026 ± 0.002 μμg. radium, while the total radium present in the combined original samples was 76.0 μμg. The radium held by the precipitates was insignificant.

When fifty milligrams each of chromium(III), chromium(VI), and titanium (with 0.57 gram potassium dihydrogen phosphate added) were carried through the working procedure, no difficulties were experienced. Chromium(III) was oxidized in about twenty minutes in the fusion process; The resultant chromium(VI) was reduced again by the hydrogen peroxide. Titanium phosphate was not precipitated in the presence of hydrogen peroxide. Peroxide also dissolved any hydrated manganese dioxide which precipitated shortly after the melt was dissolved in dilute sulfuric acid.

When two hundred milligrams each of calcium, iron(III), aluminum, uranium, and magnesium were carried separately through the entire procedure (with 0.57 gram potassium dihydrogen phosphate added), only iron(III) and calcium caused difficulty. Because of the slight solubility of calcium sulfate, the calcium test sample had to be kept hot during filtration. The iron test sample required the addition of hydrochloric acid at Step 3 to yield a clear solution. This difficulty with iron has never been observed with actual silicate samples.

In another test, one hundred milligrams of antimony(V), chromium(III), chromium(VI), molybdenum(VI), bismuth, vanadium(V), and tungsten(VI) were carried separately through the entire procedure except for the fusion. Flux was used to neutralize the acid in order to simulate the solution of a fused sample. No potassium dihydrogen phosphate was used. In this test, only tungsten precipitated in the final solution; however, vanadium caused difficulties in the filtration with paper, and fritted glass had to be substituted.

Performance of Method on NBS Silicates and in Other Laboratories

Replicate analyses of nine silicates certified by the National Bureau of Standards were performed. The results are shown in Table III. While our results generally agreed among themselves, agreement with the NBS certified values was not always good. Results on one half of the five-gram samples taken should have fallen within the probable error estimated by the Bureau.

TABLE III

Results of Analyses of Five-gram Samples of NBS Certified Silicates

| NBS Sample Number | Type of Sample | μμg. Ra ± Probable Error[a] per Gram of Sample | | |
|---|---|---|---|---|
| | | NBS Certified Value | Found | Average |
| 4980 | Quartzite | 0.06 ± 0.01 | 0.110 ± 0.002[b]<br>0.089 ± 0.002<br>0.085 ± 0.001 | 0.095 ± 0.001 (0.009)[a] |
| 4976 | Carthage Limestone | 0.15 ± 0.03 | 0.094 ± 0.002[b,c]<br>0.093 ± 0.001[b]<br>0.107 ± 0.002 | 0.100 ± 0.001 (0.009)[a] |
| 4984 | Triassic Diabase | 0.18 ± 0.03 | 0.153 ± 0.002[b]<br>0.161 ± 0.002 | 0.157 ± 0.001 (0.004)[a] |
| 4983 | Milford Granite | 0.23 ± 0.02 | 0.283 ± 0.003[b]<br>0.267 ± 0.003 | 0.275 ± 0.002 (0.008)[a] |
| 4977 | Berea Sandstone | 0.24 ± 0.02 | 0.264 ± 0.002[b]<br>0.273 ± 0.002 | 0.269 ± 0.002 (0.004)[a] |
| 4978 | Columbia River Basalt | 0.33 ± 0.03 | 0.334 ± 0.002[b]<br>0.328 ± 0.003 | 0.331 ± 0.002 (0.003)[a] |
| 4986 | Kimberlite | 0.59 ± 0.04 | 0.751 ± 0.004[b]<br>0.758 ± 0.005 | 0.755 ± 0.003 (0.003)[a] |
| 4979 | Chelmsford Granite | 2.96 ± 0.08 | 4.74 ± 0.02[b]<br>2.32 ± 0.01[c]<br>2.32 ± 0.01[c]<br>6.67 ± 0.01[c]<br>6.74 ± 0.02<br>2.24 ± 0.01[c]<br>2.26 ± 0.01<br>2.94 ± 0.01[c]<br>2.96 ± 0.01 | 3.79 ± 0.01 (1.28)[a] |

TABLE III (Continued)

| NBS Sample Number | Type of Sample | μμg. Ra ± Probable Error[a] per Gram of Sample | | |
|---|---|---|---|---|
| | | NBS Certified Value | Found | Average |
| 4981 | Graniteville Granite | 3.3 ± 0.2 | 3.40 ± 0.01[b] | |
| | | | 3.28 ± 0.02 | 3.34 ± 0.01 (0.06)[a] |
| Blanks | (Based on one-gram silicate sample) | | 0.018 ± 0.001[b] | |
| | | | 0.021 ± 0.001[b] | |
| | | | 0.020 ± 0.001 | |
| | | | 0.022 ± 0.001 | 0.020 ± 0.001 (0.001)[a] |

a NBS probable error includes estimate of errors due to non-homogeneity of samples. One half of the results on five-gram samples should fall within the limits of the probable error. Our probable errors are based upon the appropriate counting statistics and the P.E. of the average of the four blanks. Probable errors given in parentheses are based on variations of the individual results from the mean. Results of duplicate de-emanations of a sample were averaged and treated as one sample in the statistical computations.

b Filtered through paper; all others filtered through membrane filters.

c This value and the one following it were obtained by duplicate de-emanations of the same sample. See also note a.

TABLE III (Continued)

| NBS Sample Number | Type of Sample | μμg. Ra ± Probable Error[a] per Gram of Sample | | |
|---|---|---|---|---|
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| 4981 | Graniteville Granite | 3.3 ± 0.2 | 3.40 ± 0.01[b]<br>3.28 ± 0.02 | 3.34 ± 0.01 (0.06)[a] |
| Blanks | (Based on one-gram silicate sample) | | 0.018 ± 0.001[b]<br>0.021 ± 0.001[b]<br>0.020 ± 0.001<br>0.022 ± 0.001 | 0.020 ± 0.001 (0.001)[a] |

a NBS probable error includes estimate of errors due to non-homogeneity of samples. One half of the results on five-gram samples should fall within the limits of the probable error. Our probable errors are based upon the appropriate counting statistics and the P.E. of the average of the four blanks. Probable errors given in parentheses are based on variations of the individual results from the mean. Results of duplicate de-emanations of a sample were averaged and treated as one sample in the statistical computations.

b Filtered through paper; all others filtered through membrane filters.

c This value and the one following it were obtained by duplicate de-emanations of the same sample. See also note a.

In evaluating the results, the following factors should be considered:

1. The authors' method determines total radium if the flux decomposes all minerals. No insoluble residues were observed in any of the solutions of samples.
2. The authors' method is theoretically sound, since it uses the highly efficient coprecipitation with a large amount of barium sulfate and normally entirely decomposes the sample.
3. The data presented for all samples, except No. 4979, are internally quite consistent. Results higher and lower than the certified values were obtained, which indicates no trend to higher or lower values such as might occur if the standard radium solutions were in error.
4. The absolute amounts of radium measured were in the range 0.47 - 33 µµg. and were measured against consistent blanks of 0.1 µµg. This indicates freedom from contamination. Sample No. 4979 was one of two granites both of which were quite high in radium content. Errors in measuring these amounts of radon should not have been over ±2.5%. Duplicate de-emanations of the same bubbler indicate smaller errors. Excellent agreement internally and with the certified value was obtained on the second granite sample (No. 4981). It is unlikely that 33 µµg. of radium could be found in a sample containing only 15 µµg. by a chemist experienced in radium analysis using the method described.

5. The five replicate analyses on sample No. 4979 were done independently in three different batches by two chemists; The last three replicates were done in one batch.
6. It is implied in the NBS circular (8) that the "cold emanation" method could have been used by some of the cooperating analysts in establishing the certified values. Such a method could not give total radium results unless the radon could readily diffuse out of the minerals present.

Table IV gives the results obtained in three laboratories by the method as applied to routine samples. The samples were prepared and furnished by the authors. In general, the agreement is very good for routine samples considering the levels of activity involved.

Blanks and Sensitivity of Method

In our experience with the method, blanks ranged from about 0.02 to 0.07 μμg. radium per sample when 8 grams of flux and 100 mg. of barium were used. The data in Table III indicate that the flux contained no more than 0.02 μμg. radium per 8 grams of flux. Analyses of various lots of barium salts indicated that as much as 0.03 μμg. radium per 100 mg. barium may be present. About 0.01 μμg. radium was found in the quantity of phosphoric acid used. By fractional crystallization of the barium chloride, it was possible to get the total blank down to about 0.03 μμg. radium. For example, when purified barium chloride was used, 16 blanks run with 16 batches of routine samples over a period of 10 months averaged 0.028 μμg. radium; ranged from 0.008 to 0.039 μμg. radium; and had a standard deviation of 0.009 μμg. radium. This standard

TABLE IV

Results of Routine Analyses of Silicates by Proposed Method in Three Laboratories

| Sample No. | (μμg. Ra ± σ[a])/g. Dry Sample | | | Sample No. | (μμg. Ra ± σ[a])/g. Dry Sample | | Sample No. | (μμg. Ra ± σ[a])/g. Dry Sample | |
|---|---|---|---|---|---|---|---|---|---|
| | Lab 1[b] | Lab 2[c] | Lab 3[d] | | Lab 1[b] | Lab 2[c] | | Lab 1[b] | Lab 2[c] |
| 213 | 55.2 ± 0.8 | 56.4 ± 0.6<br>54.0 ± 0.5 | -- | 678 | 1.07 ± 0.02 | 1.26 ± 0.06<br>1.09 ± 0.06 | 730 | 2.00 ± 0.03 | 2.0 ± 0.1<br>2.18 ± 0.06 |
| 380 | 6.3 ± 0.1 | -- | 6.5 ± 0.1 | 679 | 24.5 ± 0.4[e]<br>25.6 ± 0.5[e]<br>24.1 ± 0.5[f] | 16.8 ± 0.2 | 733 | 2.91 ± 0.04 | 2.93 ± 0.08<br>2.54 ± 0.08 |
| 387 | 1.78 ± 0.03 | -- | 1.88 ± 0.04 | 687 | 1.16 ± 0.02 | 1.12 ± 0.06<br>1.01 ± 0.07 | 749 | 11.2 ± 0.2 | 11.2 ± 0.2<br>10.4 ± 0.2 |
| 391 | 2.95 ± 0.06 | -- | 2.88 ± 0.05 | 697 | 7.1 ± 0.3 | 7.6 ± 0.2 | 751 | 277 ± 3 | 250 ± 1 |
| 412 | 8.7 ± 0.2 | -- | 9.0 ± 0.2 | 702 | 1.11 ± 0.02 | 0.98 ± 0.06<br>1.01 ± 0.05 | 760 | 1.72 ± 0.02 | 1.62 ± 0.08<br>1.57 ± 0.08 |
| 415 | 34.2 ± 0.5 | -- | 34.0 ± 0.3 | 720 | 2.20 ± 0.03 | 1.95 ± 0.06<br>2.37 ± 0.07 | 769 | 74 ± 1[e]<br>71 ± 1[e]<br>76 ± 1[f] | 68.1 ± 0.6<br>67.7 ± 0.6 |
| 427 | 34.5 ± 0.5 | -- | 34.6 ± 0.4 | 726 | 0.77 ± 0.02 | 0.63 ± 0.04<br>0.79 ± 0.05 | 800 | 11.2 ± 0.2 | 11.1 ± 0.2<br>11.4 ± 0.2 |
| 442 | 22.0 ± 0.3 | -- | 19.9 ± 0.3 | | | | | | |
| 601 | 7.1 ± 0.2 | 7.3 ± 0.2 | -- | | | | | | |
| 603 | 0.64 ± 0.01 | 0.54 ± 0.04 | -- | | | | | | |

a σ based on counting statistics only.
b Authors' analyses. Sample Nos. 213 through 603 were done by hot digestion; all others were done by the cold digestion option.
c Commercial laboratory. Used cold digestion option. Different techniques and equipment were used for counting radon. Duplicate results are on separate portions of sample; these were submitted to laboratory as separate samples.
d Analyses by Dr. S. D. Shearer of the Public Health Service, working at the University of Wisconsin. NBS standard radium solutions for calibration furnished by authors. Used cold digestion.
e Replicate de-emanations of same bubbler.
f Repeated analysis from same sample.

deviation was based on the individual variations of the values from the mean. The standard deviation of the group was 0.004 μμg. radium when it was based on counting statistics alone. All of the reagents could be purified if the need arose.

The magnitude and variability of the blank, cell backgrounds, and counting statistics determine the minimum amount of radium which can be determined. As a guide, the writers consider 0.05 μμc. to be the practical lower limit of detection for radium and radon. Experiments aimed at lowering the blanks are in progress.

## DISCUSSION

### Radioactive Interferences

If an emanation method is used for the radium determination, actinon(radon-219) and thoron(radon-220) are theoretical interferences. Practically, their effects usually can be ignored unless the samples are very much out of radioactive equilibrium. Even so, the problem can be solved fairly easily. If no special provisions are made for thoron and actinon, they will appear as 0.6% and 0.1% (maxima), respectively, of their curie equivalents of radon-222, assuming that the radon samples are aged four hours and counted one hour. If counted (or aged) overnight, the interferences drop to 0.4% and 0.00% (maxima), respectively. In samples suspected of having high radium-223 to radium-226 ratios, no noticeable effects from actinon have been observed (11).

If an emanation method is not to be used, further purification of the barium-radium sulfate will be required. The method described by Wamser et al. is applicable with slight modification to the phosphoric

acid melt. From our experience, phosphoric acid solutions of radium are usually difficult to free from radioactive interferences. Hence a different technique for getting the barium-radium sulfate back into solution may be advisable (e.g., metathesis with sodium carbonate followed by solution of the barium-radium carbonate in dilute HCl).

Application to Other Types of Samples

The general method can be used on most liquids such as liquids and effluents from uranium mills. Slight modifications are needed to be sure that the barium sulfate precipitation is quantitative.

Solid samples other than silicates, i.e., uranium and vanadium concentrates, probably can be handled by the method without prior solution in acid. The general method, with suitable modifications, has been used successfully by the writers on samples of algae, insects, vegetables, bone, and fish. Often relatively large samples (500 grams live weight) of vegetables are needed to obtain the required sensitivity. Up to five grams of bone ash have been handled with a loss of 0.4% by increasing the precipitation volume. The writers have used five-gram samples of silicates by increasing the flux, reagents (except barium), and volumes (up to Step 7) by a factor of five.

The same general type of flux, like alkali fluorides, has been in limited use for decades but many chemists do not seem to be familiar with it. It is useful in chemical or radiochemical analyses of silicates where extractions, precipitations, redox reactions, or colorimetric work need to be done in strongly acid solutions in which silicic acid would ordinarily interfere. The general approach might, for example,

be used to determine strontium-90 in silicates by precipitation with stable strontium as the sulfate, to extract certain metals (e.g., Fe, As, etc.) from silicates with solvents or solvents plus organic reagents, to precipitate zirconyl phosphate, to determine titanium as the colored peroxy complex, and to determine iron by redox reactions (9). The barium sulfate is omitted if the flux is to be used for such purposes. Mineral acids other than sulfuric can be used with the flux when indicated by chemical considerations, if equivalent amounts are used.

## SUMMARY

The rapid method which has been described is suitable for the separation and determination of radium in silicates which are decomposed by fusion with sodium carbonate-potassium carbonate-sodium tetraborate flux. The radium determination itself is done most suitably by the emanation method, but under appropriate circumstances other methods could be used. It is possible to handle large silicate samples, since the radium is coprecipitated with barium sulfate and separated from the bulk of the common elements. Satisfactory recoveries (average 99.5%, range of 97 - 102%) of added radium were obtained from several types of silicates and from samples containing calcium, titanium, zirconium, tin, niobium, and tantalum in reasonable amounts. Most other common elements cause no difficulties.

Likely chemical interferences have been checked. Zirconium in large amounts presents a problem in that it precipitates, but it has been shown that a large precipitate carries very little radium. Radiochemical interferences depend upon the method used for the final radium

determination. The method efficiently collects radium and gets it into a freely emanating form. The slight errors involved are chiefly the errors in the radon measurements.

Seven out of twenty-two results on NBS certified samples were within the probable error ranges estimated by the NBS. In general, the other fifteen results tended to be higher than the certified values. Comparative analyses with two other laboratories were satisfactory.

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# DETERMINATION OF RADIUM-226
## Preparation and Analysis of Special Types of Samples

by
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## ORES, TAILINGS, SEDIMENTS, AND OTHER SILICATES

Analyze by method given for silicates.

## REFRACTORY SILICATES

Occasional samples may contain minerals which do not yield to the special flux used in the silicate method. Such samples or unattacked residues may be fused with a suitable amount of KF-NaF mixture (1:1). The fusion is conveniently done in a platinum dish. The melt is treated with excess dilute sulfuric and evaporated to fumes to remove fluoride. Rinse down sides of dish and evaporate to heavy fumes. Dilute and proceed with the precipitation of the barium-radium sulfate.

The flux has a tendency to stretch platinum and should be used in small amounts so that thin layers are involved. Almost all inorganic substances are decomposed by the fluoride flux.

## DUSTS

1. Ash filter, on which sample is collected, in platinum crucible.
2. Proceed as in method for silicates. Reduce amount of flux if desired. If reduction is made in amount of flux, an equivalent amount of $H_2SO_4$ should be subtracted from the volume of $H_2SO_4$ used in Step 3.

## WATER

1. Filter water through a membrane filter. Add 2% by volume of HCl.
2. Transfer 1020 ml. of the acidified sample to a 1500-ml. beaker. Add with stirring 50 ml. $BaCl_2$ solution (2 mg. $Ba^{++}$/ml.). Add with stirring 20 ml. concentrated sulfuric acid, cover, let stand overnight.
3. Continue as in method for silicates beginning with Step 6.

## URINE

1. Sample should be acidified with 2 to 5% by volume HCl or $HNO_3$ soon after the sample is voided. If radium only is to be determined, $HNO_3$ is preferable; if uranium is to be determined on same sample, HCl must be used.
2. Add 100 mg. $Ba^{++}$ as carrier and wet ash 200 ml. of urine with 20 ml. $H_2SO_4$ and 20 ml. $HNO_3$. Small additional amounts of $HNO_3$ will usually be required to complete the ashing. (Larger urine samples may be used if the acids are increased proportionately.)
3. Dilute the ashed sample to the volume of the original urine sample. (Dilute more if much calcium sulfate is present as will be the case with a urine having a high specific gravity. With such an amount of barium carrier, losses will be insignificant.) Note approximate amount of silica present in order to judge amount of HF needed in a later step.
4. Cover and digest overnight on steam bath (to convert polyphosphates to orthophosphate).
5. Continue as in method for silicates, beginning with Step 6. Filtration while hot is quite permissible. Increase amount of HF used in Step 7, if such increase appears necessary.

## URANIUM MILL PROCESS SOLUTIONS AND EFFLUENTS

Process solutions and effluents may contain organic material, silica, and vanadium. Precipitates are likely to form during storage no matter whether the sample is acidified or left untreated. For this reason, it is best to filter the sample immediately, take a suitable aliquot, and proceed with the analysis. If the analysis cannot be started immediately, the aliquot should be preserved in a glass bottle or in the container in which the analysis is to be started. If stored in a bottle, precipitates must be redissolved before proceeding with the analysis.

While chemical methods may need to be modified somewhat depending upon the composition of the sample, the procedure given will work with most samples:

1. Add 100 mg. $Ba^{++}$ and wet ash sample (50 to 100 ml.) with nitric and sulfuric acids as outlined for urine. (The volume of sulfuric may have to be increased if the sample has a high concentration of dissolved solids.)
2. Proceed as in method for urine. (Some samples will have a very large silica content and will require a large volume of HF for its volatilization.)

## BIOLOGICAL SAMPLES
## (VEGETATION, ALGAE, INSECTS, TISSUE, BLOOD, FECES, AND BONE)

Biological samples, other than blood or urine, usually contain silicates as accidental contaminants and these must be gotten into solution because in a radium analysis no insoluble residue may be

discarded without danger of losing a large part of the radium. For this reason, such contaminants become an integral part of the sample and the analytical method must be chosen to handle such substances. This means that a fusion ordinarily is required for samples such as feces, vegetables, bone, aquatic biota, fish flesh, meats, and the like. Where the amount of silicates is small, a treatment with HF may replace satisfactorily the fusion procedure.

Ordinary elements such as iron, aluminum, calcium, silicon, and phosphorus may cause special problems in certain types of large (500 g.) biological samples, while in other types of samples there may be little or no problem. This fact makes it impossible to write a procedure which will handle any type of large sample and, at the same time, will be as simple as it could be for less complicated samples. Aside from the wide variations in chemical compositions of biological ashes, there are very great differences in the behavior of various types of samples in ashing processes. For the reasons outlined above, a considerable amount of judgment is needed in planning the analysis in order to make it as simple as possible for the particular samples to be analyzed.

The steps in analyzing biological samples are as follows:

1. Dry ash at 500° C. in platinum dish or porcelain casserole. (If salts fuse, the temperature is too high. With some samples, the ash will be free from carbon; usually, carbon will be present.)
2. Digest ash on steam bath in covered casserole for 30 minutes with 25 ml. 1:1 HCl. Dilute to about 200 ml. and filter through No. 42 paper. Wash paper about eight times with hot dilute

1:99 HCl. If the residue contains only a little carbon and a small amount of silica and silicates, transfer it to a platinum crucible and ash in a muffle furnace at 500° C. If the residue is large and mostly carbon, return it to the original vessel, ash at 500° C., repeat the digestion with acid (using less), dilute, filter, and wash. Repeat the ashing, etc., if necessary, until almost all the carbon is burned off and then transfer the final filter paper and residue to a platinum crucible and ash in a muffle furnace.

3. If the inorganic ash from Step 2 weighs one gram or less, it can be fused with 8 grams of special flux and reserved for addition later to the filtrate (Step 5). If over 1 gram of silicates is present, increase the weight of flux proportionately (also increase $H_2SO_4$ volume in Step 4). If the ash weighs more than a gram and consists mostly of silica (rather than silicates), treatment with HF and $H_2SO_4$ is advantageous.
4. To the rinsed and dried casserole (Step 2), add 20 ml. concentrated $H_2SO_4$, heat to fuming, and rub $H_2SO_4$ up sides with a glass rod to remove radium. Repeat rubbing process and continue fuming for about 15 minutes. Cool and <u>cautiously</u> add to filtrate obtained in Step 2.
5. Evaporate the combined filtrates to fumes of $SO_3$ to remove HCl, dilute to 200 ml. and add the crucible which contains the fusion of the insoluble material from Step 3. After the melt dissolves,

remove crucible, rinse, and reserve for use later in procedure. Digest on steam bath for 1 hour to dissolve difficultly soluble sulfates of iron, aluminum, etc.

6. Add 5 ml. 3% $H_2O_2$, dilute to approximately 1 liter, and heat to boiling. (The solution should be essentially clear.) Add slowly with vigorous stirring 50 ml. $BaCl_2$ solution (2 mg. $Ba^{++}$/ml.). Cover and digest cold overnight or hot for 1 hour (if much calcium is present).
7. Continue analysis as in method for silicates, beginning with Step 6 of that procedure.

Ashes of algae, insects, and small bone samples (ca. 1 gram) may be fused directly with flux as described for silicates. Because of its high calcium content, a large bone sample is most easily handled by a special procedure. If the precipitation, digestion, and filtration are done hot, the above procedure can handle about 5 grams of bone. If $CaSO_4$ does precipitate with the final barium sulfate, the latter may be purified by reprecipitation from sulfuric acid. A few milligrams of $CaSO_4$ does no harm.

BONE (SPECIAL METHOD)

The following method is written for approximately 5 g. (ashed weight) bone:

1. Dry ash bone at 500° C.; cool. Add 50 ml. $BaCl_2$ (2 mg. $Ba^{++}$/ml.) and 50 ml. concentrated HCl. Cover and digest until sample is essentially dissolved. Add with stirring 1 ml. 1:9 $H_2SO_4$.
2. Remove cover and evaporate on steam bath to remove most of HCl.

3. Add 50 ml. 1% HCl, cover, digest on steam bath, and filter with immersion fritted glass filter. Discard filtrate.
4. Reverse-flush filter into original vessel, add more 1% HCl (25 to 50 ml. as judged necessary), and repeat digestion and filtration. Wash residue with small portions of hot 1% HCl. Discard filtrate and washings.
5. With uncontaminated bone, the $BaSO_4$ residue may be treated with HF and $H_3PO_4$ immediately. If silicates are present, fuse in platinum with special flux and follow the method for silicates, omitting the addition of $BaCl_2$.

## RADIUM LOSSES AND OTHER ERRORS

The various methods described are extremely efficient in collecting radium. Analyses of filtrates indicate the following losses:

1. Method for ores - 0.2%
2. Method for water and urine - 0.1%
3. Special method for bone (5-g. sample) - 0.15%
4. Fusion method for bone (5-g. sample) - 0.5%
5. Biological samples, general method - 0.5% (est.)

Larger errors in recovery arise when the radon is determined by scintillation counting. Such errors are about ±2.5% under optimum conditions. These errors are <u>not</u> due to statistical errors of counting, but are inherent in the scintillation determination of radon.

# DETERMINATION OF POLONIUM-210

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## GENERAL

Methods based on two different principles are given for polonium-210. Deposition on silver (or other metals, such as copper, stainless steel, nickel, or Monel metal) is widely used for simple samples (e.g., water and urine) (1, 2, 3). The method also may be useful for preparing polonium for counting after separation by some other means.

Coprecipitation with selenium or tellurium by stannous chloride may be carried out in strong hydrochloric acid solutions and is very effective, because very few elements precipitate under the same conditions. Both selenium and tellurium can be precipitated by other reagents which do not precipitate polonium (4, 5). Hence, they may be separated from polonium after they have served their functions as collectors. Selenium is readily volatilized by repeated evaporations with hydrobromic acid. The literature states that polonium will deposit on elemental tellurium, but this is difficult to reconcile with the fact that tellurium can be precipitated as the element without precipitating polonium. The methods are particularly useful in separating polonium from complex samples. The author's experience with these methods has been limited to effluents and urine. Experience with the selenium method is more limited than the experience with the tellurium method.

## PRELIMINARY PREPARATION OF SAMPLES

Several precautions are necessary in handling polonium solutions or samples:

1. Polonium is volatile at relatively low temperatures when dry and dry-ashing procedures are not permissible (1a).
2. Polonium tends to form radiocolloids and special precautions are necessary in transferring and storing standard solutions as well as samples.
3. Polonium deposits on metals, so that platinum vessels cannot be used.

Samples of a biological nature are wet ashed with nitric and perchloric acid or with nitric acid alone (1a, 3). Nitric acid is undesirable in both methods described but a small amount can be tolerated. Removal of nitric acid by fuming with perchloric is effective and satisfactory in the deposition method. Sulfuric acid is permissible in the selenium and tellurium coprecipitation methods and is satisfactory for removing nitric acid.

Silica may be removed by evaporation with HF and $H_2SO_4$ in Teflon® vessels. In the selenium or tellurium coprecipitation method, it is more convenient to remove silica after the first precipitation of the selenium (or tellurium) if the sample contains much salts. The silica should be dehydrated before the precipitation to be sure that it will be filterable. The same Teflon® vessel should be used for the dehydration and for the other subsequent operations to avoid losses from transfers.

The sulfuric acid used in wet ashing urine (10 ml. $H_2SO_4$ per 100 ml. urine) does not interfere with the selenium or tellurium coprecipitation.

PROCEDURE FOR SELENIUM COPRECIPITATION IN ABSENCE OF $HNO_3$ AND SILICA (4)

1. Add 0.1 mg. $Pb^{++}$ and 0.1 mg. $Bi^{+++}$.
2. Add 1 mg. $Se^{++}$.
3. Adjust volume to 100 ml.; adjust HCl concentration to 3N. Add 5 ml. 10% $SnCl_2 \cdot 2H_2O$ (in 3N HCl) in excess of that needed to start precipitation. Cover and digest over live steam for one hour. Cool in water and immediately filter by suction through a fine fritted glass immersion filter. Wash twice with 3N HCl containing 2 ml. 10% $SnCl_2 \cdot 2H_2O$/liter. Remove the washings from the beaker and immersion filter as well as possible.
4. Reverse-flush the filter with 3N HCl plus bromine to dissolve precipitate. Use pressure from rubber bulb to force solution through filter. Rinse inside and outside of filter into sample. (Clean filter by drawing water through it; finally rinse with 3N HCl + $SnCl_2$ wash solution and reserve for use in Step 6A, 6B, or 6D.)
5. Add 1 ml. HBr and evaporate to dryness on a boiling steam bath. Repeat HBr treatment and evaporation until Se volatilizes. Continue analysis according to one of the following alternatives:

6A. Dissolve residue in hot 3N HCl and proceed with Steps 2 through 5. Dissolve final residue in a few ml. 1:3 nitric, warm to expel any chlorides or bromides, transfer to stainless steel planchet and evaporate under an infrared lamp. Count alpha particles in a proportional or scintillation counter.

6B. Same as 6A but make no attempt to remove selenium.

6C. Dissolve residue in 17 ml. hot 3N HCl, dilute to 100 ml., transfer to silver-foil plating apparatus with 0.5N HCl. Plate for 90 minutes (1d). Count as described under 6A.

6D. Dissolve residue in 33 ml. hot 3N HCl, add 0.1 mg. Te (see Step 6C in tellurium procedure), dilute to 100 ml., and proceed as directed for coprecipitation with Te, Steps 3 through 6A, 6B, 6C, or 6D.

7. Correct for decay, if correction is required and applicable. See Table I.

PROCEDURE FOR TELLURIUM COPRECIPITATION IN ABSENCE OF $HNO_3$ AND SILICA (4)

1. Add 0.1 mg. Pb(II) and 0.1 mg. Bi(III).
2. Add 1 mg. or 0.1 mg. Te(IV). (See Step 6C.)
3. Adjust volume to 100 ml.; adjust HCl concentration to 1N. Add 5 ml. 10% $SnCl_2 \cdot 2H_2O$ (in 3N HCl) in excess of that needed to start precipitation. Cover and digest over live steam for one hour. Cool in water and immediately filter by suction through a fine fritted glass immersion filter. Wash twice with 1N HCl containing 2 ml. 10% $SnCl_2 \cdot 2H_2O$/liter. Remove the washings from the beakers and filter as well as possible.
4. Same as Step 4 in selenium procedure except that 1N HCl-Br and 1N HCl-$SnCl_2$ are used instead of the 3N reagents. For rinsings into sample, use 1N HCl instead of water.
5. Continue analysis according to one of the following alternatives:

TABLE I

The Decay of Polonium-210 in Days and Hours

($\lambda$ = 0.005,008,289 per day)

| Time, t | $e^{-\lambda t}$ | | Time, t | $e^{-\lambda t}$ | |
|---|---|---|---|---|---|
| | Hours | Days | | Hours | Days |
| 0 | 1.000 000 | 1.000 000 | | | |
| 1 | 0.999 791 | 0.995 004 | 40 | 0.991 688 | 0.818 459 |
| 2 | 0.999 583 | 0.990 033 | 50 | 0.989 620 | 0.778 478 |
| 3 | 0.999 374 | 0.985 087 | 60 | 0.987 557 | 0.740 450 |
| 4 | 0.999 166 | 0.980 166 | 70 | 0.985 499 | 0.704 279 |
| 5 | 0.998 957 | 0.975 269 | 80 | 0.983 444 | 0.669 876 |
| 6 | 0.998 749 | 0.970 397 | 90 | 0.981 394 | 0.637 153 |
| 7 | 0.998 540 | 0.965 549 | 100 | 0.979 348 | 0.606 028 |
| 8 | 0.998 332 | 0.960 726 | 110 | 0.977 307 | 0.576 424 |
| 9 | 0.998 124 | 0.955 926 | 120 | 0.975 269 | 0.548 266 |
| 10 | 0.997 915 | 0.951 151 | 130 | 0.973 236 | 0.521 484 |
| 11 | 0.997 707 | 0.946 399 | 140 | 0.971 208 | 0.496 009 |
| 12 | 0.997 499 | 0.941 671 | 150 | 0.969 183 | 0.471 780 |
| 13 | 0.997 291 | 0.936 966 | 160 | 0.967 163 | 0.448 733 |
| 14 | 0.997 083 | 0.932 286 | 170 | 0.965 146 | 0.426 813 |
| 15 | 0.996 875 | 0.927 628 | 180 | 0.963 135 | 0.405 963 |
| 16 | 0.996 667 | 0.922 994 | 190 | 0.961 127 | 0.386 132 |
| 17 | 0.996 459 | 0.918 383 | 200 | 0.959 123 | 0.367 270 |
| 18 | 0.996 251 | 0.913 795 | 210 | 0.957 124 | 0.349 329 |
| 19 | 0.996 043 | 0.909 230 | 220 | 0.955 129 | 0.332 265 |
| 20 | 0.995 835 | 0.904 687 | 230 | 0.953 137 | 0.316 034 |
| 21 | 0.995 627 | 0.900 168 | 240 | 0.951 151 | 0.300 596 |
| 22 | 0.995 420 | 0.895 671 | 250 | 0.949 168 | 0.285 912 |
| 23 | 0.995 212 | 0.891 196 | 260 | 0.947 189 | 0.271 945 |
| 24 | 0.995 004 | 0.886 744 | 270 | 0.945 215 | 0.258 661 |
| 25 | 0.994 797 | 0.882 314 | 280 | 0.943 244 | 0.246 025 |
| 26 | 0.994 589 | 0.887 906 | 290 | 0.941 278 | 0.234 007 |
| 27 | 0.994 381 | 0.873 520 | 300 | 0.939 316 | 0.222 576 |
| 28 | 0.994 174 | 0.869 156 | 310 | 0.937 358 | 0.211 703 |
| 29 | 0.993 967 | 0.864 814 | 320 | 0.935 404 | 0.201 362 |
| 30 | 0.993 759 | 0.860 494 | 330 | 0.933 454 | 0.191 525 |

6A. Adjust volume to 100 ml. with 1N HCl. Boil to remove all but trace of bromine. Proceed as in Steps 3 through 4. Evaporate to dryness on steam bath. Dissolve final residue in a few ml. of 1:3 $HNO_3$, warm to expel bromides and chlorides, transfer to a stainless steel planchet and evaporate under an infrared lamp. Count alpha particles in a proportional counter or scintillation counter.

6B. Remove tellurium by precipitation with hydrazine hydrochloride. Filter, adjust acidity of filtrate, and plate on silver foil (1d).

6C. Evaporate solution to dryness, dissolve residue in 17 ml. hot 3N HCl, dilute to 100 ml., transfer to silver-foil plating apparatus with 0.5N HCl. Plate for 90 minutes (1d). Count as described under 6A. (The tellurium may interfere by flaking off the silver foil. If this alternative is to be carried out, it would be better to use 0.1 mg. Te in Step 2.)

6D. Reprecipitate the tellurium as in Step 3, but filter on membrane filter. Transfer membrane filter to planchet. Tack down with trace of solvent, dry, spray with conducting coating, dry, and count.

7. Correct for decay, if correction is required and applicable. See Table I.

PROCEDURE FOR DEPOSITION ON SILVER FOIL INCLUDING ASHING (URINE) (1c, 3)

1. The urine sample should be made strongly acidic (10% by volume of HCl or $HNO_3$) soon after it is voided. Nitric acid is preferable unless uranium is to be run on same sample. If nitric acid is used

for acidifying, the addition of the initial nitric acid in the next step is not necessary. A sample volume of 200 ml. is suitable.

2. To the urine sample, add 10% by volume of $HNO_3$. Evaporate nearly to dryness on a hot plate. Add 10 ml. $HNO_3$ and 20 ml. $HClO_4$ (60%). Evaporate until nitric acid is removed and $HClO_4$ fumes are evident. If solution darkens, add a few drops of $HNO_3$. Cover and place on a hot plate at about 200° C. Watch to see if solution darkens. If it does, add a few drops of $HNO_3$ to oxidize organic matter. When solution can be heated without appreciable darkening, let it digest for 30 minutes. Cool.
3. Add 25 ml. water and evaporate on a low-temperature hot plate to fumes of $HClO_4$. (This step is to remove chlorine dioxide and other oxidants.)
4. Cool, add 50 ml. chlorine-free water, and neutralize with NaOH pellets (or strong solution). Use litmus paper as an external indicator. Add enough HCl to give a 0.5N solution when the sample is diluted to the final volume (ca. 160 ml.) used in plating.
5. Transfer solution to the plating cell, dilute to 160 ml., and plate with mechanical stirring for 90 minutes. The plating cell is immersed in boiling water and the time is counted after the solution has reached its maximum temperature.
6. Remove silver foil and rinse with chlorine-free water. Dry foil at room temperature or in oven at 110° C. for a few minutes.
7. Count foil in low-level alpha counter. Correct count for decay if such correction is applicable. See Table I.

To check recovery, run spiked aliquots of sample.

## INTERFERENCES

None of the other naturally occurring polonium isotopes has a half-life greater than 3.05 minutes. Since at least a day is required for any of the chemical methods, all isotopes except polonium-210 will have decayed to insignificance during the analysis. All lead radionuclides are beta emitters and would not interfere, except through growth of decay products, if they accompanied the polonium-210. Both alpha and beta emitters occur among the isotopes of bismuth; of these only Bi-212 has a half-life long enough (60.5 min.) to cause any interference if it accompanied the polonium-210.

In the selenium and tellurium coprecipitation methods, satisfactory separations are known (to the author) to be made from thorium, uranium, radium, bismuth, lead, and radon. The only other natural alpha emitter is protactinium-231 which occurs in the actinium series. It seems unlikely that protactinium-231 would interfere.

Of the stable elements, iron(III) is the most common interference in the silver plating method. Its interference can be eliminated by reducing it with ascorbic acid (1d). Selenium and tellurium color the silver but do not interfere with the deposition of polonium unless they are present in abnormal amounts. Silver, nickel, copper, and nitrate ions prevent complete deposition of polonium. If other metals, less noble than silver, are used for the plating, elements such as bismuth, antimony, and lead would be expected to deposit.

To the author's knowledge, common elements do not prevent coprecipitation of polonium with selenium and tellurium when stannous chloride is used as the precipitant, but enough reagent must be used to reduce elements like iron, vanadium, and chromium.

## RECOVERY

The deposition of polonium on silver foil varies from 85 - 100% and appears to be affected by a large number of variables. The recovery of polonium from ashed urine is about 98 - 100% with the selenium and tellurium coprecipitation methods.

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